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(71) Applicant: RAYCHEM CORPORATION
300 Constitution Drive
Menlo Park California 94025(US)

(72) Inventor: Aune, Ted M.
37481 Rockwood Drive
Fremont California 94536(US)

(72) Inventor: Germeraad, Paul Blake
2002San Mateo Drive
Menlo Park California 94025(US)

(72) Inventor: Chan, Randolph Winston
577 Taylor Street
Sunnyvale California 94086(US)

(74) Representative: Auckland, Jacqueline et al,
Raychem Limited Swan House 37-39, High Holborn
London WC1(GB)

(54) **Electrical sheet heaters.**

(57) An electrical heater which comprises a fabric prepared from the electrodes and an elongate resistive heating element which is composed of a conductive polymer, preferably a PTC conductive polymer, to render the heater self-regulating. The fabric is laminated to, and preferably embedded in, a sheet of an insulating polymer, particularly a non-tracking insulating polymer.

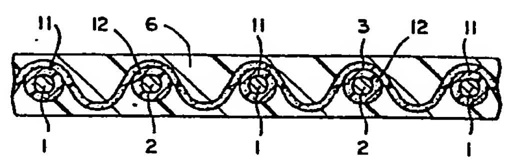

FIG_2

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Croydon Printing Company Ltd.

This invention relates to electrical sheet heaters comprising conductive polymers.

The term "conductive polymer" is used herein to denote a composition which comprises a polymeric component and, dispersed (or otherwise distributed) in the polymeric component, a sufficient amount of a conductive filler to render the composition electrically conductive. Conductive polymers, which may exhibit PTC (positive temperature coefficient) or ZTC (zero temperature coefficient) including NTC (negative temperature coefficient) behavior, are well known. Reference may be made, for example, to U.S. Patent Nos. 2,952,761; 2,978,665; 3,243,753; 3,351,882; 3,571,777; 3,757,086; 3,793,716; 3,823,217; 3,858,144; 3,861,029; 3,950,604; 4,017,715; 4,072,848; 4,085,286; 4,117,312; 4,177,376; 4,177,446; 4,188,276; 4,237,441; 4,242,573; 4,246,468; 4,250,400; 4,252,692, 4,255,698, 4,271,350, 4,272,471, 4,304,987, 4,309,596, 4,309,597, 4,314,230, 4,314,231, 4,315,237, 4,317,027, 4,318,881, 4,327,351, 4,330,704, 4,334,351, 4,352,083, 4,361,799, 4,388,607, 4,398,084, 4,413,301, 4,425,397, 4,426,339, 4,426,633, 4,427,877, 4,435,639, 4,429,216, 4,442,139, 4,459,473, 4,473,450, 4,481,498, 4,502,929, 4,514,620, 4,517,449, 4,529,866, 4,534,889, and 4,560,498; J. Applied Polymer Science 19, 813-815 (1975), Klason and Kubat; Polymer Engineering and Science 18, 649-653 (1978), Narkis et al; and European Application Nos. 38,713, 38,714, 38,718; 74,281, 92,406, 119,807, 134,145, 84,304,502.2, 84,307,984.9, 85,300,415.8, 85,306,476.4 and 85,306,477.2.

Our European Application No. 84 307984.9 (Publication No. 0 144 187) discloses that a wide range of electrical heaters can be easily and economically manufactured through the application (or adaptation) of known fabric-making techniques (particularly weaving, but including also, for example, knitting and braiding) to manufacture heaters which comprise elongate elements of at least two different types, one type comprising one of the electrodes and the other type (or one of the other types, if there are three or more different types) comprising a component composed of a material having a relatively high resistivity. Generally both the electrodes are in the form of elongate elements which form part of the same fabric.

In the further development of the heaters of the prior application, and of other fabric heaters comprising elongate elements having outer surfaces which are composed of a conductive polymer and across which current flows, we have found that the performance of such heaters can deteriorate substantially, particularly when the heater has been subjected to flexing, apparently due to increases in contact resistance and/or to physical separation of the conductive elements. We have found that the performance of such heaters can be improved by laminating at least one, and preferably both, of the faces of the fabric heater to a layer of insulating polymeric material with the aid of heat under conditions such that (1) the polymeric material flows into the fabric heater and (2) the outer surfaces of said elongate elements are deformed to provide improved electrical contact with

adjacent surfaces, e.g. of wire electrodes. The conditions used in the lamination must not be such as to cause excessive melting or flowing of the conductive polymer which would interfere with the desired performance of the heater. Thus the insulating material should melt at a temperature lower than the conductive polymer (and, if necessary, be cross-linked after the lamination step so that it does not flow during use of the heater) and/or the conductive polymer should be cross-linked prior to the lamination, in order to prevent excessive deformation of the conductive polymer during the lamination. Particularly useful heaters are obtained when the insulating material is a non-tracking material, as described for example in U.S. Patent Nos. 4,399,604 and 4,470,898, the disclosures of which are incorporated herein by reference.

In one aspect the present invention provides an electrical sheet heater which comprises

(1) a fabric comprising a plurality of elongate elements which are interlaced together in an ordered array, said elongate elements comprising

(a) a plurality of first electrodes which are substantially parallel to each other, and which are electrically connected to each other;

(b) a plurality of second electrodes which are substantially parallel to each other

and to the first electrodes, which are electrically connected to each other, and which are spaced apart from the first electrodes; and

(c) a plurality of resistive heating elements which are composed of a conductive polymer, which are substantially parallel to each other and at an angle to the electrodes, and through which current passes when the first and second electrodes are connected to a power source;

(2) means for connecting the first electrodes and second electrodes to a power source; and

(3) a laminar matrix which is composed of an electrically insulating material comprising an organic polymer and within which said fabric (1) is embedded.

A preferred process for making such a heater comprises

(1) weaving the fabric from elongate elements which comprise

(a) in a first direction, the first electrodes, the second electrodes, and elongate elements which are composed of a thermoplastic, electrically insulating material comprising an organic polymer

and which lie between the first and second electrodes, and

(b) in a second direction, elongate elements which are composed of a conductive polymer and elongate elements composed of a thermoplastic, electrically insulating material comprising an organic polymer;

(2) placing the fabric between two sheets which are composed of a thermoplastic, electrically insulating material comprising an organic polymer; and

(3) applying heat and pressure to the sheets and the fabric so that thermoplastic materials soften and flow to form the laminar matrix having the fabric embedded therein.

The electrodes used in this invention are usually of metal, e.g. copper or nickel-coated copper, for example a solid or stranded wire. In one preferred class of heaters, at least one of the electrodes is electrically surrounded by a PTC element preferably a PTC conductive polymer element. Usually the PTC element will be melt-shaped, preferably melt-extruded, preferably so that it physically surrounds the electrode as a uniform coating throughout its length; however, other methods of forming the PTC element, e.g. dip-coating, and other geometric arrangements, are possible. In other preferred heaters, the fabric comprises an elongate resistive element which compri-

ses, and preferably consists essentially of, a PTC material, preferably a fibrous element (mono-filament or multifilament) made by melt-extruding a PTC conductive polymer. The PTC fiber or coating can vary in thickness and/or resistivity radially and/or longitudinally. Alternatively, the PTC element can alternate radially and/or longitudinally with polymeric elements having different electrical properties, e.g. which exhibit a different type of PTC behavior, which are electrically insulating, or which have a resistance which is much higher than the resistance of the PTC element at room temperature, so that at least when the device is at relatively low temperatures, substantially all the current between the electrodes passes through the PTC element. The PTC element can be in direct physical contact with the electrode or can be separated therefrom by a layer of ZTC material, for example a low resistivity conductive polymer, which may be applied to the electrode as a conductive paint. The dimensions of the PTC element and the resistivity and other properties of the PTC composition should be correlated with the other elements of the device, but those skilled in the art will have no difficulty, having regard to their own knowledge (e.g. in the documents referenced herein) and the disclosure herein, in selecting suitable PTC elements. Suitable polymers include polyethylene and other polyolefins; copolymers of one or more olefins with one or more polar comonomers e.g. ethylene/vinyl acetate, ethylene/acrylic acid and ethylene/ethylacrylate copolymers; fluoropolymers, e.g. polyvinylidene fluoride and ethylene/tetrafluoroethylene copolymers; and polyarylene polymers, e.g. polyether ketones; and

mixtures of such polymers with each other and/or with elastomers to improve their physical properties.

The heaters can also comprise an elongate ZTC conductive polymer element. This ZTC element can be of uniform composition or can comprise discrete sub-elements; for example it may be desirable to coat an electrode or a PTC element surrounding an electrode with a first ZTC conductive polymer in order to provide improved electrical and physical contact to a second ZTC conductive polymer. Alternatively or additionally a ZTC material can be coated on the junctions between the elongate elements to provide improved electrical contact. The dimensions of the ZTC electrical element and the resistivity and other properties of the ZTC conductive polymers preferably used for it should be correlated with the other elements of the device, but those skilled in the art will have no difficulty, having regard to their own knowledge (e.g. in the documents referenced herein) and the disclosure herein, in selecting suitable ZTC elements. Suitable polymers for the ZTC material include copolymers of ethylene with one or more polar copolymers, e.g. ethyl acrylate and vinyl acetate.

The elongate elements can be formed into a fabric by any method which results in an ordered array of interlaced elongate elements. Weaving is the preferred method, but knitting, braiding etc. can be used in suitable cases. When it is stated herein that the first and second electrodes are "substantially parallel" to each other, this includes localized

variation from a strictly parallel configuration such as is present for example in a knitted fabric. Similarly when it is stated that other elements are substantially at right angles to the electrodes, this includes localized variation from such a configuration. The density of the weave (or other form of interlacing) can be selected in order to provide the desired power output or other property. Similarly, the density of the weave can be varied from one area to another to provide a desired variation, eg. of at least 10% or at least 25%, in one or more properties from one discrete area (which may be, for example, at least 5% or at least 15% of the total area) to another. Triaxial weaving can be employed.

In order to pass current through the device, the electrodes must of course be connected to a power source, which may be DC or AC, e.g. relatively low voltage, e.g. 12, 24 or 48 volts, or conventional line voltages of 110, 220, 440 or 600 volts. The various components of the device must be selected with a view to the power source to be employed. When the electrodes are elongate electrodes, they may be powered from one end or from a number of points along their lengths; the former is easier to provide, but the latter results in more uniform power generation.

The heater prior to lamination may include, at least in selected areas thereof, a non-conductive element, which may be an interlaced elongate element, which provides desired properties during the lamination (eg. by melting and flowing, or assisting satisfactory

lamination) and/or in the final product, eg. an elongate element composed of glass fibers, which provides stiffness or other desired physical properties, or composed of a non-tracking material in order to inhibit the deleterious effects of arcing. The heater can be laminated to, or can comprise, thermally responsive member, for example a layer of a hot melt adhesive or a mastic; a thermochromic paint; or a component which foams when heated.

The electrodes generally run in one direction in the fabric (which may be the warp or the weft, depending on the ease of weaving). The electrodes can be powered from one end, in which case they will normally have a serpentine shape and be insulated from each other at the cross-over points. Alternatively the fabric can be woven so that each of the electrodes is or can be exposed at regular intervals along the fabric, eg. each time it changes direction, thus permitting the exposed portions to be bussed together by some bussing means which permits the desired shrinkage to take place. Generally, the exposed portions of the first electrodes will be joined together along one edge of the fabric and the exposed ends of the second electrodes will be joined together along the opposite edge of the fabric.

The thermal properties of the device and of the surroundings are important in determining the behavior of the device. Thus the device can comprise, or be used in conjunction with, a thermal element which helps to spread heat uniformly over the device, eg. a metal

foil layer, or which reduces the rate at which heat is removed from the device, eg. a layer of thermal insulation such as a foamed polymer layer.

The fabric may be laminated with a material to render it impermeable, to strengthen it, to improve heat dissipation or otherwise to alter its electrical or physical properties. Instead of or in addition to such lamination, a material may be applied to improve electrical contact between the first and second electrodes on the one hand and the resistive element on the other hand. A suitable material for this purpose comprises a conductive paint. Electrical contact may also be improved by subjecting the fabric or the laminate to compression, for example by passing it through nip rollers.

One may alter the electrical properties of the heater by incorporating into it two or more PTC materials having different temperature coefficients of resistance. For example, one PTC material may be present as a PTC fiber and another as a jacket encasing a wire electrode. Alternatively the heater can contain a PTC fiber comprising two or more materials having different temperature coefficients of resistance, e.g. a PTC fiber in tape form whose orientation is fixed relative to electrodes with which it is interlaced. Tape-like fibers have the advantage of increased contact area with the electrodes. Thus the tape may comprise a strip of material having a high switching temperature (a temperature or range of temperatures at which a substantial change in resistivity occurs) lami-

nated to a strip of material having a lower switching temperature. Such a tape can be interlaced as part of a fabric such that, say, the material of lower switching temperature contacts only phase electrodes and the material of higher switching temperature contacts only neutral electrodes. The result is a much sharper switching temperature than would be achieved if either of the materials were used separately.

Referring now to the drawing, Figure 1 is a diagrammatic, partial cross-sectional side view of a heater which is suitable for lamination to sheets of non-conductive polymeric material in order to make a heater of the invention. It shows electrodes 1 of one polarity, each surrounded by a ZTC conductive polymer element 11, and parallel electrodes 2 of opposite polarity, each surrounded by a ZTC conductive polymer element 21. The electrodes are woven into a fabric with non-conductive, non-tracking filaments 4 between them, and with PTC filaments 3 and non-conductive non-tracking filaments 5 at right angles to them.

Figure 2 is a diagrammatic partial cross-sectional side view of the device of Figure 1 after it has been laminated between two sheets of the same non-conductive, non-tracking material as the filaments 4 and 5, under conditions which cause the sheets and the filaments to melt and coalesce to form a matrix 6 in which the fabric heater is embedded.

The invention is illustrated by the following Example.

EXAMPLE

The non-tracking material used in this Example comprised ion oxide and alumina trihydrate dispersed in an ethylene/vinyl acetate copolymer, as described in U.S. Patent No. 4,399,064. The filaments of this material were 0.020 inch in diameter. The PTC conductive polymer filaments were 0.040 inch in diameter and were prepared by melt extruding a composition which comprises carbon black dispersed in high density polyethylene. the electrodes were nickel-coated copper stranded wires which were 0.020 inch in diameter and were coated with a thin ZTC layer of a graphite-containing polymer thick film ink.

A fabric was woven, with the coated electrodes separated by non-tracking filaments running in one direction, and PTC filaments separated by non-tracking filaments running at right angles to the first direction. The center-to-center separation of adjacent electrodes was 0.25 inch, with a single non-tracking filament midway between them. The center-to-center separation of adjacent PTC filaments was 0.125 inch, with a single non-tracking filament midway between them.

A sample of the fabric was placed between two sheets of the non-tracking material, each 0.15 inch thick, leaving the edges of the fabric exposed, and the

assembly was pressed at about 275°F and a pressure of about 25 psi for about 5 minutes, thus causing the filaments and sheets of the non-tracking material to melt and coalesce into a substantially continuous matrix of the material. The resulting structure was then irradiated to a dose of about 5 Mrad.

Alternate conductors on one of the exposed edges of the laminate were connected to a busbar which was insulated from the other conductors. The other conductors were connected to a second busbar on the other exposed edge. When the busbars were connected to a power source, current passed between the conductors through the PTC filaments, thus generating heat.

EXAMPLE 2

A PTC fiber having a diameter of 0.04 inch was made by melt-extruding a PTC conductive polymer composition comprising carbon black dispersed in a mixture of polyethylene and an ethylene/ethyl acrylate copolymer, followed by irradiation to a dosage of about 7 Mrads to cross-link the polymer. A fabric was then woven in which the warp consisted of commercially available rayon fibers and, at intervals of 0.4 inch, three contiguous wires, each a 30 AWG nickel-coated copper solid wire which had been coated with a conductive paint containing graphite (Electrodag 502), and the weft consisted of the same rayon fibers and, at intervals of about 0.11 inch, a PTC fiber prepared as described above.

The resulting fabric was placed between two sheets of an ethylene/propylene rubber (sold by Uniroyal under the trade name TPR 8222B) and the assembly was laminated between silicone pads at 450°F for one minute, using minimum pressure.

The resulting product was trimmed, and the wires exposed along the edges of the heater. The heater had a stable resistance and a low Linearity Ratio (ratio of resistance at 100 volts AC to resistance at 0.04 volts AC) of less than 1.1, even after flexing.

CLAIMS

1. An electrical sheet heater which comprises

(1) a fabric comprising a plurality of elongate elements which are interlaced together in an ordered array, said elongate elements comprising

(a) a plurality of first electrodes which are substantially parallel to each other, and which are electrically connected to each other;

(b) a plurality of second electrodes which are substantially parallel to each other and to the first electrodes, which are electrically connected to each other, and which are spaced apart from the first electrodes; and

(c) a plurality of resistive heating elements which are composed of a conductive polymer, which are substantially parallel to each other and at an angle to the electrodes, and through which current passes when the first and second electrodes are connected to a power source;

(2) means for connecting the first electrodes and second electrodes to a power source; and

(3) a laminar matrix which is composed of an electrically insulating material comprising an

organic polymer and within which said fabric (1) is embedded.

2. A heater according to claim 1 wherein at least the first electrodes comprise a metal conductor which is coated by a conductive polymer exhibiting ZTC behavior.

3. A heater according to claim 1 or 2 wherein the heating elements comprise a conductive polymer exhibiting PTC behavior.

4. A heater according to claim 1 or 2 wherein the heating elements are in the form of filaments which are composed of a conductive polymer exhibiting PTC behavior and which run in a direction substantially at right angles to the electrodes.

5. A heater according to claim 1 wherein at least the first electrodes comprise a metal conductor which is coated by a conductive polymer exhibiting PTC behavior.

6. A heater according to claim 5 wherein the heating elements are in the form of filaments which are composed of a conductive polymer exhibiting ZTC behavior and which run in a direction substantially at right angles to the electrodes.

7. A heater according to any one of claims 3 to 6 wherein the electrically insulating material has a melting point lower than the T_s of the PTC conductive polymer and has been cross-linked.

8. A heater according to any one of claims 3 to 6 wherein the electrically insulating material has a melting point higher than the T_s of the PTC conductive polymer and the PTC conductive polymer has been cross-linked.

9. A heater according to any one of the preceding claims wherein the electrically insulating material contains an anti-tracking material, preferably alumina trihydrate.

10. A method of making a heater as claimed in any one of the preceding claims which comprises

(1) weaving the fabric from elongate elements which comprise

(a) in a first direction, the first electrodes, the second electrodes, and elongate elements which are composed of a thermoplastic, electrically insulating material comprising an organic polymer and which lie between the first and second electrodes, and

(b) in a second direction, elongate elements which are composed of a conductive polymer and elongate elements composed of a thermoplastic, electrically insulating material comprising an organic polymer;

(2) placing the fabric between two sheets which are composed of a thermoplastic, electrically

insulating material comprising an organic polymer; and

(3) applying heat and pressure to the sheets and the fabric so that thermoplastic materials soften and flow to form the laminar matrix having the fabric embedded therein.

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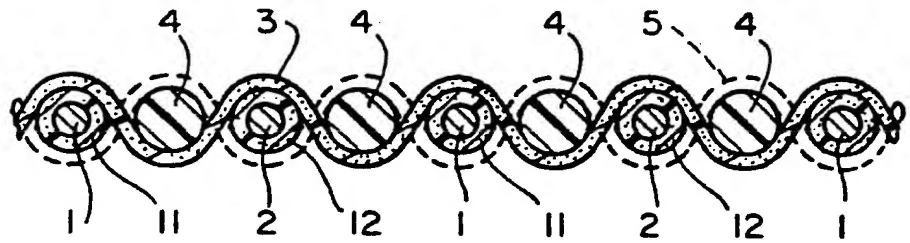

FIG_1

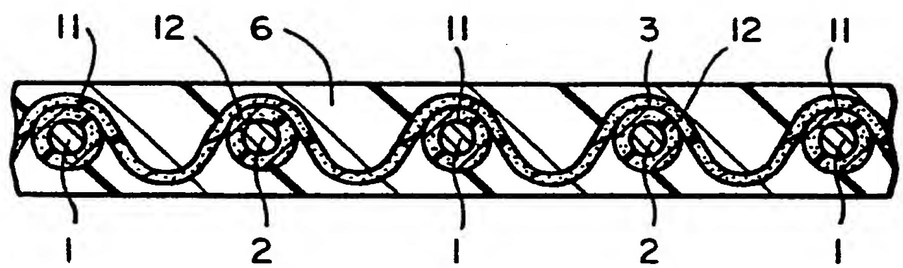

FIG_2

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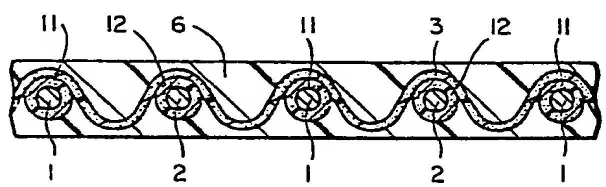
(71) Applicant: RAYCHEM CORPORATION, 300 Constitution Drive, Menlo Park California 94025 (US)

(72) Inventor: Aune, Ted M., 37481 Rockwood Drive, Fremont California 94536 (US)
Inventor: Germeraad, Paul Blake, 2002San Mateo Drive, Menlo Park California 94025 (US)
Inventor: Chan, Randolph Winston, 577 Taylor Street, Sunnyvale California 94086 (US)

(74) Representative: Auckland, Jacqueline et al, I.P.L.D. Raychem Limited Swan House 37-39, High Holborn, London WC1 (GB)

(54) Electrical sheet heaters.

(57) An electrical heater which comprises a fabric prepared from the electrodes and an elongate resistive heating element which is composed of a conductive polymer, preferably a PTC conductive polymer, to render the heater self-regulating. The fabric is laminated to, and preferably embedded in, a sheet of an insulating polymer, particularly a non-tracking insulating polymer.



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EUROPEAN SEARCH REPORT

0202896

Application Number

EP 86 30 3765

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,E	EP-A-0 144 187 (RAYCHEM CORP.) * abstract, figures 1, 2, 4; claims 1-10 * ---	1,10	H 05 B 3/36 H 05 B 3/14
Y	FR-A-2 340 016 (ICI LTD.) * page 1, line 35 - page 2, line 33; page 4, lines 9-27; claim 12 * ---	1,2-6, 10	
Y	DE-A-2 749 601 (KORN) * figure; page 7, line 9 - page 8, line 1 * ---	1,2-6, 10	
Y	US-A-4 444 708 (G.M. GALE) * abstract, figure 1, column 7, line 57 - column 8, line 5 * ---	2-6	
A	EP-A-0 040 537 (RAYCHEM CORP.) * abstract; figure 1; claims 1-10; page 8, line 25 - page 9, line 13 * ---	1,3-5,7 -9	
A	GB-A-2 089 851 (FIBERITE CORP.) * abstract; figure 1; page 2, lines 20-112 * ---	4,6	**TECHNICAL FIELDS SEARCHED (Int. Cl.4)**
A	EP-A-0 138 424 (RAYCHEM CORP.) * page 3, page 4, line 14; page 7, line 23 - page 8, line 27 * ---	3,4,7-9	H 05 B
A	US-A-4 421 582 (D.A. HORSMA et al.) * abstract; figures 2, 4; column 1, line 60 - column 2, line 44; column 2, line 56 - column 4, line 56 * -----	1,3-5,7 -9,10	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	04-12-1987	BECKER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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